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X. "Photochemical Researches." By Prof. BUNSEN and HENRY E. ROSCOE, B.A., Ph.D. 3rd Communication. "The Optical and Chemical Extinction of the Chemical Rays." Communicated by Professor STOKES, Sec. R.S. Received May 20, 1857.

(Abstract.)

In order to determine whether the act of photochemical combination necessitates the production of a certain amount of mechanical effect, for which an equivalent quantity of light is expended, or whether this phenomenon is dependent upon a restoration of equilibrium effected without any corresponding equivalent loss of light, we must now study the phenomena occurring at the bounding surfaces, and in the interior of a medium exposed to the chemically active rays.

If I_0 represents the amount of light entering a medium, and I the amount issuing from the medium, we have $\alpha I_0 = I$, when α represents the fraction of the original amount of light which passes through the medium, on the supposition that the light extinguished is proportional to the original intensity of the light. The first series of experiments was made with the view of determining this point. The intensity of the chemical rays proceeding from a constant source of light was measured before and after passage through a cylinder with plate-glass ends, filled with dry chlorine. The amount of transmitted light, I , was determined for various intensities of incident light, I_0 , and the fraction $\frac{I}{I_0}$ was found to remain constant, proving that the absorption of the chemical rays varies directly as the intensity of the light. From this result, the general law of the extinction of the optical and chemical rays in transparent media may be deduced. For, as it has been shown that the amount of light transmitted through a medium of finite thickness is proportional to the intensity of the incident light, it may be assumed that this same relation will hold good for an infinitely thin medium. According to this supposition, the relation between the transmitted light, I , and the thickness of the medium, is represented by the equation $I = I_0 \cdot 10^{-h\alpha}$ and $\alpha = \frac{1}{h} \log \left(\frac{I_0}{I} \right)$, in which I_0 represents the light before transmission, I , that after transmission through a layer of h thickness, and $\frac{1}{\alpha}$ the thickness of absorbing

medium by passing through which the amount of light has diminished to $\frac{1}{10}$ th.

The difference between the incident and transmitted light, *i. e.* that lost in passing through the medium, is made up (1) of a portion reflected, and (2) of a portion absorbed or extinguished. We have experimentally determined the values of the coefficient of reflexion ζ , and the coefficient of extinction α , for the glass plates used in our cylinders. We found that 4.86 per cent. of the chemical rays, from a flame of coal-gas, which fall perpendicularly on a surface of crown glass, are lost by the first reflexion; and that the amount of light absorbed in our plates was so small as to fall within the limits of observational errors. The value of ρ for the plates of glass employed was found to be 0.0509. When the coefficient of reflexion for glass ρ is known, the amount of light α transmitted by n plates is found from the formula $\frac{1-\rho}{1+(2n-1)\rho} = \alpha$. Hence the amount of light transmitted by two plates is 0.823. We have confirmed the accuracy of the calculated result by direct experiment, and obtained a value 0.800, or a mean of 0.811 as the coefficient of transmission of our plates.

If all the transparent media have not the same coefficient of reflexion, the order in which the media are placed will affect the amount of transmitted light. We have given an example of the mode in which the calculation must in this case be made, in the determination of the coefficient of extinction of water. We found that the amount of light absorbed by a column of water 80 millimetres thick was inappreciable. According to the method here adopted, it is possible to determine the coefficient of reflexion of all transparent fluids for the chemical rays. We have only determined the coefficient of reflexion for American mica; for the chemical rays of a coal-gas flame ρ was found to be = 0.1017. From the coefficient of reflexion, the refractive index (i) can be calculated from the equation $\rho = \left(\frac{1-i}{1+i}\right)^2$ or $i = \frac{1-\sqrt{\rho}}{1+\sqrt{\rho}}$. The refractive index for crown glass thus calculated from $\rho = 0.0509$ is found to be $i = 1.583$; the refractive index for Fraunhofer's line H has been optically determined to be between 1.5466 and 1.5794 (Buff's Physik).

Another important element in the investigation of photochemical extinction is the law according to which the optical coefficient of

extinction varies with the density of the absorbing medium. A series of experiments proved that the amount of chemical rays transmitted through a medium varies proportionally with the density of the absorbing medium.

We may now proceed to the investigation of the original question proposed, viz.—in the combination of chlorine and hydrogen effected by the light, are the chemical rays expended in a relation proportional to the quantity of hydrochloric acid formed? The first point to be determined, in order to answer this question, is the coefficient of extinction of pure chlorine for the chemical rays of a coal-gas flame. The amount of light was measured before and after transmission through cylinders filled with chlorine. The loss of light by reflexion $\alpha = 0.811$ must be deducted from the incident light, and then the coefficient of extinction for chlorine is calculated. From a series of determinations, the value of $\frac{1}{\alpha}$, *i. e.* the depth of chlorine at 0° C. and 0.76 pressure, through which the light must pass in order to be reduced to $\frac{1}{10}$, is found to be, as a mean of five experiments, 171.7 mm. Another series of determinations were made with chlorine diluted with air, in order to prove experimentally that the absorbed light varies in the case of chlorine directly as the density. The quantity of chlorine contained was determined in each instance by a volumetric analysis. An average of six experiments gave a value for $\frac{1}{\alpha} = 174.3$ mm. As a mean of these two series of experiments we have a value of 173.3.

If the light is not consumed in the act of photochemical change, the coefficient just found must remain unaltered when the chlorine and hydrogen mixture is employed; if on the contrary light is not only lost by the optical extinction, but an amount of light vanishes proportional to the chemical action, experiment must give a larger value for the coefficient.

In order to determine this important question we employed an apparatus (fully described in the Paper), by means of which we could expose columns of the sensitive gas of various lengths, to a constant source of light. By determining the amount of action effected in these columns of varying length, we are able to obtain the value of the coefficient of extinction for the sensitive mixture. A series of experiments showed that when the light had passed through

234 millimetres of the sensitive mixture of chlorine and hydrogen at 0° and 0.76, it was reduced to $\frac{1}{10}$ of its original intensity. If, instead of hydrogen, we had diluted the chlorine with some other transparent but chemically inactive gas, the depth to which the rays must penetrate in order to be reduced to $\frac{1}{10}$ is according to the experiments with pure chlorine, 346 millimetres. Hence it is seen that for a given amount of chemical action effected in the mixture of chlorine and hydrogen, an equivalent quantity of light is absorbed. For we find that in the case of the standard chlorine and hydrogen mixture, where, together with the optical absorption, a chemical action of the light occurs, the value of the coefficient of extinction is 0.00427; whereas in the chlorine mixture of similar dilution, where the chemical action was absent, the coefficient is found to be 0.00289, or very much smaller.

It appeared of great interest to repeat these experiments with rays from other luminous sources. For this purpose we employed the diffuse light of morning reflected from the zenith of a cloudless sky. The experiments gave a value of $\frac{1}{\beta}$ of 45.6 mm. for chlorine. That is, diffuse morning light was reduced to $\frac{1}{10}$ by passing through 45.6 millimetres of chlorine. A series of experiments made with our apparatus and the standard mixture gave a depth of 73.5 millimetres of chlorine and hydrogen before the light was reduced to $\frac{1}{10}$. From this it is seen that morning zenith light is much more easily absorbed by chlorine than lamp-light. Hence it was conjectured that the diffuse solar light might differ in its properties in this respect with the time of day or year. Experiment fully confirmed this supposition. Observations made with evening light proved that a depth of 19.7 mm. of chlorine was sufficient to reduce the light to $\frac{1}{10}$ of its original amount, and that 57.4 mm. of the standard mixture was required to effect the same end.

The conclusion which we draw from all our observations is, that the coefficients of extinction of pure chlorine for chemical rays from various sources of light are very different. The depth to which such light must penetrate chlorine at 0° and 0.76, in order to be reduced to $\frac{1}{10}$ of its original intensity, is—

- (1.) For a flame of coal-gas 173.3 mm.
- (2.) Reflected zenith light, morning 45.6 mm.
- (3.) Reflected zenith light, evening 19.7 mm.

Hence it is seen that the chemical rays reflected at different times and hours not only possess quantitative but also qualitative differences, similar to the various coloured rays of the visible spectrum. Had nature endowed us with the power of discriminating the chemical rays, as we do the visible ones, by impressions of varying colour, we should see the rosy tints of morning pass in the course of the day through all the gradations of colour until the warm evening ones at length succeed.

A long and continued series of observations must be made before we are able to appreciate the influence which these qualitative differences in the chemical rays exert upon the photochemical phenomena of vegetation. That this influence must be of the greatest importance is evident from the varying effects produced in other photochemical processes by differences in the solar light. We need only mention in proof of this assertion, the fact, well known to all photographers, that the amount of light, photometrically speaking, gives no measure for the time in which a given photochemical effect is produced, and that a less intense morning light is always preferred for the preparation of pictures to a bright evening light.

XI. "On the Causes and Phenomena of the Repulsion of Water from the Feathers of Water-Fowl and the Leaves of Plants."

By GEORGE BUIST, D.C.L. of Bombay, F.R.S. Received April 3, 1857.

Happening to reside in Bombay, in the neighbourhood of a number of small tanks or ponds abounding with the Lotus or sacred bean of India, and with four different varieties of Water Lily, I was struck with the different appearances presented by these when immersed in water, or when water was sprinkled on them. The leaves of the lily, like those of the Lotus, floated with considerable buoyancy on the surface, but never, like the Lotus, rose above it, on a tall independent stem. The lily leaf is full of holes about the size of a pin's head, and serrated at the edges. Through these, when the leaf is pressed down, the water perforates freely. The upper surface of the leaf is smooth and shining, and water runs off it without wetting it, as it does off a piece of glass or greased surface. When